

Low Temperature Waste Form for Supplemental Immobilization of Hanford Low Activity Waste – 17485

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ABSTRACT

The Hanford site has approximately 56 million gallons of radioactive waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being constructed to treat the waste but will only have sufficient capacity to treat about one-third of the Low Activity Waste (LAW) portion within the anticipated time-frame for completing the waste treatment mission. The LAW vitrification facility will need to be supplemented with additional LAW vitrification capacity or an alternate LAW immobilization technology. The LAW immobilization technologies considered must be capable of treating approximately 65% of Hanford's LAW and will be evaluated with respect to facilities required, quantity of final waste forms and secondary wastes produced, waste form performance data, technical viability, and life cycle cost and schedule estimates. A low temperature (i.e. non-thermal) waste form and treatment process is being evaluated to provide the additional LAW immobilization capacity.

Low temperature, cementitious waste forms have been evaluated previously for immobilizing Hanford tank waste but were not further developed for various reasons. Over the past few years the Hanford Tank Operations Contractor has conducted a technology development program to evaluate a low temperature waste form for immobilization of Hanford LAW including formulation development and testing with a range of simulant compositions spiked with radioactive and hazardous contaminants of concern (COCs). The objectives of this program include; developing a low temperature waste form formulation that is robust with respect to both waste form performance and processing properties over a range of LAW compositions, demonstrating waste form performance with real waste, and conducting Engineering Scale testing to advance the technical maturity of the low temperature immobilization process. The purpose of this paper is to report progress toward these objectives, in particular testing with real waste including additives to enhance technetium and iodine retention.

INTRODUCTION

About 56 million gallons of radioactive and hazardous waste are stored in 177 underground storage tanks at the U.S. Department of Energy's (DOE's) Hanford Site in southeastern Washington State. The wastes were generated during reprocessing of nuclear fuel to produce nuclear material for the national defense purposes. The Hanford Tank Waste Treatment and Immobilization Plant (WTP) is being constructed to treat the wastes and immobilize them in a glass waste form. The WTP includes a pretreatment facility to separate the wastes into a small volume of high-level waste (HLW) containing most of the radioactivity and a larger volume of low-activity waste (LAW) containing most of the nonradioactive chemicals. The HLW will be converted to glass in the HLW vitrification facility for ultimate disposal

at a federal geologic repository. At least a portion (~35%) of the LAW will be converted to glass in the LAW vitrification facility and will be disposed of onsite as low-level radioactive mixed waste (LLMW) at the Integrated Disposal Facility (IDF). The pretreatment and HLW vitrification facilities will have the capacity to treat and immobilize the wastes destined for each facility. However, supplemental LAW treatment capacity will be needed for the expected volume of LAW requiring immobilization.

A cementitious waste form known as Cast Stone is one of the technologies being evaluated to provide the required additional LAW immobilization capacity. The Cast Stone waste form and immobilization process must be tested to demonstrate that the final Cast Stone waste form can comply with the waste acceptance criteria for the disposal facility and that the immobilization processes can be controlled to consistently provide an acceptable waste form product. Further, the waste form must be tested to provide the technical basis for understanding the long-term performance of the waste form in the disposal environment. These waste form performance data sets are needed to support performance assessment (PA) analyses of the long-term environmental impact of the waste disposal in the IDF. The PA is needed to satisfy DOE Order 435.1 requirements.

Cast Stone was previously evaluated for supplemental immobilization of Hanford LAW in the early 2000s [1]. That work involved limited formulation development and focused on a single LAW composition that represented an average of much of the salt cake in Hanford Tank Waste. A development program was initiated in 2012 to test a range of anticipated Hanford LAW compositions and to advance the technical maturity of the Cast Stone waste form and immobilization process per DOE 413.3-4 guidelines. The objectives of the current program to evaluate the suitability of Cast Stone for supplemental immobilization of Hanford LAW include the following:

- Determine an acceptable formulation for the LAW Cast Stone waste form.
- Evaluate sources of dry materials for preparing the LAW Cast Stone.
- Demonstrate the robustness of the waste form over a range of LAW compositions and process variables.
- Provide Cast Stone contaminant release data suitable for PA and risk assessment evaluations.
- Demonstrate scalability of the process
- Conduct testing with actual waste

METHODS AND MATERIALS

The initial phase of development of Cast Stone for Hanford LAW was to conduct screening tests to evaluate the impact of key parameters including ranges in waste composition, waste stream concentrations, sources of dry materials, and mix ratios of waste (free water basis) to dry blend. A statistically designed test matrix was used to evaluate the effects of these key parameters on the properties of the Cast Stone as it is initially prepared and after curing. The tests were performed in FY2013 by investigators at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) with technical direction and oversight

by Washington River Protection Solutions (WRPS), the current Hanford Tank Operations Contractor to the US Department of Energy, Office of River Protection (DOE/ORP). Test methods and parameters are summarized below. Details are described in Cozzi, et. al. [2].

Simulant Compositions

For the screening tests four simulants were selected to represent a range of possible LAW compositions to be solidified in the Cast Stone waste form. They included a dissolved saltcake simulant used in previous testing of LAW immobilization technologies [1] and three simulants based on Hanford Tank Waste Operations Simulator (HTWOS) flowsheet modeling of the LAW feed that was anticipated to be sent to a supplemental LAW immobilization facility. A detailed description of the simulant development work is provided by Russell et al. [3].

Saltcake waste is a predominant form of the waste in a large number of the Single Shell Tanks (SSTs) at Hanford. To support an evaluation of supplemental treatment alternatives for Hanford LAW, a saltcake waste simulant was developed based on a blend of real waste samples from SSTs S-101, S-109, S-110, S-111, U-106, and U-109 [4]. This simulant has been used in previous Cast Stone testing with Hanford LAW stimulants and real waste and thus provides a means to tie results of current formulation development testing back to previous results. The composition matches the average composition of saltcake from 68 Hanford SSTs representing 85 percent of the total saltcake inventory in all Hanford SSTs and DSTs at that time [5].

Three additional simulants were developed based on output from the Hanford Tank Waste Operations Simulator (HTWOS) supporting the *River Protection Project System Plan*, Revision 6 [6]. The HTWOS model is used to track the tank waste as it moves from storage through retrieval, feed staging, and multiple treatment and immobilization processes over the life of the WTP mission. As one of the outputs, the HTWOS model provides the projected compositions of LAW feed to a supplemental immobilization facility over the course of the tank waste treatment mission. Three simulant compositions were selected to represent a range of LAW tank waste compositions; 1) the average composition over the entire treatment mission, 2) a composition high in dissolved Al, and 3) a high SO_4^{2-} composition. The simulant compositions selected for testing are shown in Table I.

Table I. Hanford LAW Simulant Compositions

Waste Constituent	SST Blend Saltcake	HTWOS Average	HTWOS High Al	HTWOS High SO ₄
	Concentration (moles/mole Na) ^(a)			
Na	1.000	1.000	1.000	1.000
K	0.002	0.007	0.028	-
Al	0.013	0.061	0.112	0.047
Cl	0.009	0.008	0.018	0.007
F	0.006	0.006 ^(b)	0.010	0.012 ^(b)
SO ₄	0.018	0.017	0.004	0.030
PO ₄	0.010	0.010 ^(b)	0.005	0.010 ^(b)
NO ₂	0.085	0.113	0.194	0.098
NO ₃	0.502	0.324	0.287	0.367
CO ₃	0.095	0.055	0.040	0.035
TOC Total	0.057	0.015	0.021	0.007
Free OH	0.097	0.312	0.293	0.306
(a) After charge balancing.				
(b) F and PO ₄ reduced from HTWOS values because of solids formation observed in preliminary simulants.				

The simulants were spiked with hazardous chemicals and radionuclides to determine how well the Cast Stone waste form controls the release of these constituents of concern (COCs). An initial feed vector for the RCRA metals was selected by taking the maximum weekly batch values from the HTWOS model results for the feed to supplemental LAW immobilization. An initial screen of these values showed that the levels of As, Ba, Se, Ag, Sb, Be, and Ni in the Cast Stone would be below the Universal Treatment Standards (UTS) by total analysis (i.e. Toxicity Characteristic Leaching Procedure (TCLP) [7] leachate concentrations would be below the UTS even if 100% of the COC leached).

The list of RCRA metals added and their spike levels appears in Table II. None of the COCs that fell below UTS by total analysis were added to the simulants with the exception of Ni. Nickel was included because it contributes a significant mass to the RCRA metals vector. Mercury was excluded because it forms

Table II. Spike Levels for Hazardous Constituents and Radionuclides

Waste Constituent	HTWOS Average	HTWOS Maximum	Other Considerations
RCRA Metals and UHCs ^(d)	moles/mole Na	moles/mole Na	moles/mole Na
Cd	2.78E-06	3.19E-05	-
Cr	2.42E-03	9.99E-03	4.30E-03 ^(a)
Pb	1.16E-05	5.13E-05	-
Ni	6.41E-05	6.61E-04	-
Radionuclides	Ci/mole Na	Ci/mole Na	Ci/mole Na
⁹⁹ Tc	1.13E-05	4.13E-05	-
⁹⁹ Tc ^(c)	(6.65E+02 µg/mole Na)	(2.43E+03 µg/mole Na)	-
¹²⁹ I	1.44E-08	8.01E-08	3.54E-06 ^(b)
¹²⁷ I (stable) ^(c)	(8.14E+01 µg/mole Na)	(4.53E+02 µg/mole Na)	(2.00E+04 µg/mole Na)
²³² + ²³³ + ²³⁴ + ²³⁵ + ²³⁶ + ²³⁸ U	1.59E-08	5.63E-08	-
Natural or depleted U ^(c)	-	(3.56+04 µg/mole Na)	-
(a) Cr concentration adjusted based on review of best basis inventory and previous simulants work (b) Iodine concentration increased to address possible detection limit issues in waste form leach tests. (c) These COCs were added to simulants based on mass (as shown). (d) UHCs = underlying hazardous constituents			

highly insoluble compounds with I⁻ which would decrease the ability of I⁻ to leach from the waste form. Thallium was not included because the secondary waste Cast Stone program showed satisfactory performance for TI in TCLP leach testing [8]. Thallium was also very close to the UTS value by total analysis (0.36 mg/L versus 0.2 mg/L) and thus would require minimal attenuation in TCLP leach testing to meet the UTS. The Cr spike level of 4.3×10^{-3} mole/mole Na represents the 95th percentile of HTWOS modeled compositions and is comparable to levels tested in previous work with Cast Stone for both LAW [9] and WTP liquid secondary waste [8].

To measure the retention and release of radionuclides of concern, ⁹⁹Tc, ¹²⁹I (substituted with nonradioactive ¹²⁷I), and ²³⁸U were spiked in simulants just prior to Cast Stone preparation. The ⁹⁹Tc was spiked in all samples at the HTWOS maximum concentration. Stable iodide (¹²⁷I) was spiked at 100 mg/L in the 5 M Na simulants and 156 mg/L in the 7.8 M Na simulants. These levels were chosen to increase the probability of detecting I at low concentrations during leach testing and are 44X higher than the maximum mass concentration of ¹²⁹I in Hanford LAW projected by the HTWOS model.

Screening Test Matrix

Screening tests were performed in 2013 to evaluate the effects of key parameters on the properties of the Cast Stone as it is initially prepared and after curing. The test parameters and their ranges that were investigated in the screening tests included:

- LAW simulant compositions (SST Blend, HTWOS Average, High Al, and High SO₄)
- Waste concentration (5 M and 7.8 M Na)
- Class F fly ash (FA) source Northwest (NW) = High Ca, Southeast (SE) = Low Ca
- Blast furnace slag (BFS) source (NW, SE)
- Water-to-dry-blend-solids mix ratio (0.4, 0.6).

The four simulants are described above. The Na concentrations of 5 M and 7.8 M were selected to represent a range of possible waste concentrations for processing. The Class F fly ash included a high Ca content material available in the Pacific Northwest (designated NW) and a lower Ca content material available in the Southeastern USA (designated SE). Blast furnace slags (BFSs) from the northwest (NW) and southeast (SE) were also selected for the screening tests. The 0.4 and 0.6 values of the water-to-dry-blend-solids mix ratio (mass ratio) were selected based on the range (0.35 to 0.41 water/dry mix or w/dm) used for secondary waste Cast Stone formulation work [8] and 0.60 w/dm ratio used at the Saltstone Production Facility at the Savannah River Site. The different combinations of simulants, Na concentrations, and mix ratios yielded waste loadings ranging from 9.5 wt% to 20.3 wt% total waste solids in the final Cast Stone waste form. The dry blend composition was held constant at 8 wt% portland Type I/II cement, 45 wt% Class F FA, and 47 wt% Grade 100-120 BFS [2]. A single source of ordinary portland cement (OPC) was used for all of the testing because the variability in the cement was not expected to be significant among the possible sources.

The original test matrix for the screening tests was composed of 26 test conditions. The matrix was developed using statistical optimal experimental design (OED) methods and software and included individual parameter effects as well as selected two-parameter interactions. A graphic depiction of the test matrix appears in Figure 1.

	Fly Ash Source/Blast Furnace Slag Source (Northwest or Southeast USA)							
Waste Composition	NW/NW	NW/SE	SE/NW	SE/SE	NW/NW	NW/SE	SE/NW	SE/SE
Average 5M	35	20						13 2
High SO ₄ 5M			1		10	31		
High Al 5M	28	4			24	37		17
SST Blend 5M			8		32	12		
Average 7.8M	5	29	6		27 36	3 22		
High SO ₄ 7.8M	15 25	33 38		14 7			26 21	
High Al 7.8M			19		30	9	11	
SST Blend 7.8M	16	34		18			23	
Mix Ratio (w/dm)	0.4	0.4	0.4	0.4	0.6	0.6	0.6	0.6
Original Mix No.								
Additional Mix No.			Test Combination				Replicate	

Figure 1. Cast Stone Screening Test Matrix

The matrix included five pairs of replicates to provide for quantifying the experimental and measurement uncertainties and for statistically assessing the significance of individual parameter and two-parameter interaction effects [2]. During preparation of the matrix samples, one of the laboratories discovered that the BFS source in 12 of the mixes had been inadvertently transposed (NW vs. SE). As a corrective measure, those mixes were repeated with the correct dry blend material. The mis-batched samples were retained and re-designated as Mix No.s 27 through 38.

Screening Test Sample Preparation

The Cast Stone monoliths were prepared by mixing aliquots of the simulant batches and the dry blend mixes and then casting the slurry into 2 in. × 4 in. right cylinder plastic molds to cure. To minimize the effects of inter-laboratory variation due to sample preparation, a mixing method developed by SRNL was used at both SRNL and PNNL for sample preparation. The Cast Stone mixes were prepared in approximately 1.5 Liter batches using a laboratory bench-top mixer with a specially designed impeller. Details of the mixing procedure are provided in Cozzi, et. al. [2].

After mixing, samples were taken for measuring fresh paste properties and the remaining Cast Stone material was poured into 2-in. × 4-in. cylindrical forms and capped. The capped monoliths were placed in humidified containers at 100% relative humidity and allowed to cure at room temperature for 28 days before testing.

Screening Test Fresh Paste and Cured Waste Form Properties Testing

The following fresh paste properties were measured for the 26 original and 12 additional parameter combinations:

- Flow consistency via modified ASTM D6103, *Standard Test Method for Flow Consistency of Controlled Low Strength Material (CLSM)* [10].
- Plastic viscosity via cup and bob viscometer, yield stress via vane rheometer.
- Gel time - SRNL method for time required for a mix to gel sufficiently to resist flow.
- Set time by ASTM C191 *Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle* [11] and also by monitoring for change in ultrasonic pulse velocity (UPV) as the mix cures.
- Isothermal heat of hydration in accordance with ASTM C1679, *Standard Method for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry* [12].
- Presence of free liquids at 24 hrs and after 3 days of cure time.

After curing for 28 days, the Cast Stone monoliths were characterized with respect to chemical composition, density, porosity, compressive strength, TCLP (EPA Method 1311 [7]), and contaminant leachability via EPA Method 1315 [13]. The characterization work was conducted by both PNNL and SRNL. Chemical composition was measured via standard analytical laboratory methods for sample digestion and analysis. Compressive strength was measured via ASTM C39 *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens* [14]. Cured density and porosity were measured via helium pycnometry. Detailed results are provided in Cozzi, et. al. [2] and are summarized below in the Results and Discussion section.

Cast Stone Formulation Enhancements

Following completion of the screening tests, WRPS engaged SRNL and PNNL to evaluate enhancements to the Cast Stone formulation for supplemental LAW immobilization. In FY2014 SRNL developed a test matrix to investigate additives to reduce porosity (Xypex, Silica Fume) and a mid-range water/dry mix ratio of 0.5. The matrix is shown in Figure 2. Details of the testing program are provided in Cozzi, et. al. [15]. Cast Stone samples were characterized for fresh paste and cured specimen properties with particular emphasis on performance in the EPA 1315 leach test. Results are summarized below in the Results and Discussion section.

Waste Composition	Fly Ash Source / Blast Furnace Slag Source (Northwest or Southeast USA)									
	NW/NW	SE/SE	NW/NW	NW/NW + Xypex	NW/NW + SF	SE/SE	NW/NW	NW/NW + Xypex	NW/NW + SF	SE/SE
Average 7.8M	5		51	52	61	53	54	55	62	56
SST Blend 7.8M	16	18	57	58	63	64	59	60	65	66
Mix Ratio (w/dm)	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.6	0.6	0.6
Mix No.	Screening Test Mix					Replicate				
Tc Spike		SF = Silica Fume								

Figure 2. Formulation Enhancements Matrix

Cast Stone Extended Leach Testing

Also in FY2014, PNNL initiated a program of extended duration leach testing of Cast Stone monoliths made from simulants spiked with different levels of ⁹⁹Tc and ¹²⁷I. Several suites of Cast Stone monoliths were tested beginning with selected mixes from the FY2013 screening tests which had remained exposed to leachates in the EPA Method 1315 test beyond the initial 63 day leach interval. These are referred to as the Extended Suite. Selected monoliths from the screening tests that had cured for ~7 months were subjected to leach testing beginning in FY2014 known as the Archive Suite. Two new suites of monoliths were prepared, one containing varying levels of iodide spikes known as the Iodide Suite and another containing a non-pertechnetate species known as the Tc gluconate Suite. All but the Extended Suite were exposed to both de-ionized water (DIW) and simulated vadose zone pore water (VZPW) leachants.

The monoliths in each suite were leached for the following durations; Extended Suite - 1040 days, Archive Suite and Tc-gluconate Suite – 850 days, and Iodide Suite - 570 days. Details of the extended duration leach testing and results are provided in Serne, et. al. [16] and Asmussen, et. al. [17]. Results are summarized below in the Results and Discussion section.

Engineering Scale Demonstration

In an effort to demonstrate a higher technology readiness level (TRL) in accordance with DOE Technology Readiness Assessment (TRA) guidelines, SRNL conducted an Engineering Scale Demonstration of the Cast Stone process with simulated Hanford LAW. In early FY2014 SRNL used their scaled continuous processing facility equipment to mix and pour Cast Stone into a polyethylene tank to form a large monolith 8.5 ft. in diameter by 40 in. high. SRNL collected samples from the mixer and pour stream and prepared bench scale monoliths using the same procedure that was used for the screening and formulation development tests. Details of the demonstration procedure are provided in Cozzi, et. al. [18]. Results are summarized below in the Results and Discussion section.

Cast Stone Testing with Tc and I Getters

The last phase of testing with Cast Stone for supplemental immobilization of Hanford LAW was conducted during FY2015/2016. During this time-frame PNNL conducted tests of candidate materials for improving the retention of ⁹⁹Tc and ¹²⁹I in the Cast Stone waste form, referred to as "getters". The screening tests identified Sn(II)Apatite (Sn-A) and potassium metal sulfide (KMS-2) as successful Tc getters [19,20] and Ag-exchanged zeolite (Ag-Z) and argentite (Ag₂S) as successful I getters [21]. Following the screening tests, PNNL devised a matrix for testing these getters incorporated into Cast Stone monoliths made from LAW simulants spiked with Tc and I tracers. The final test matrix for evaluating Tc and I getters in Cast Stone monoliths appears in Table III. Details of the testing are provided in Asmussen, et. al. [22].

Table III. Cast Stone Formulations for Testing with Tc and I Getters

Batch ID	6.5M Na LAW Ave. Simulant (g)	LAW Simulant Spikes	Total Dry Ingredients & Getters Used (g)	Blast Furnace Slag (g)	Fly Ash (g)	OPC (g)	Type and Mass (g) of Tc Getter	Type and Mass (g) of I Getter or I source
T1	1307.9	none	1750	822.5	787.5	140	none	none
T2	1307.9	Tc & I	1757.25	798.3	764.3	135.9	Sn-A 50.0	Ag-Z 8.75
T3	1307.9	Tc & I	1750	820.7	785.8	139.7	KMS-2-SS 2.35	Ag-Z 1.45
T4	1307.9	Tc & I	1744.95	816.7	781.9	139	KMS-2-SS 2.35	Arg 5.00
T5	1307.9	Tc & I	1750	820.7	785.8	139.7	KMS-2-SS 2.35	Ag-Z 1.45
T6	1307.9	Tc & I	1747.55	818.9	782.3	139	KMS-2-SS 2.35	Arg 5.00
T7	654.0	AgI	875.1	411.3	393.75	70.0	none	AgI 0.0198 g

Based on the results of the screening tests by PNNL and initial observations of the Tc and I getter tests, SRNL prepared samples of real waste from Savannah River Site (SRS) Tank 50 for testing Cast Stone with Tc and I getters. The Tank 50 sample was chemically adjusted to closely match the HTWOS Average LAW simulant composition. The concentration was at the lower end of concentrations tested during the Cast Stone screening tests at 5 M Na. Chromium was not spiked so as to better measure the ability of the Tc getters to reduce soluble Tc⁺⁷ to much less soluble Tc⁺⁴ species. The same getter materials used in the PNNL test matrix were used for real waste testing with some variations in addition ratios.

RESULTS AND DISCUSSION

Highlights of the results of the various phases of Cast Stone development and testing are presented in this section. References to the test reports containing the details of the testing and the supporting data and results are also provided.

Cast Stone Screening Test Results

Nearly all of the mixes yielded fresh paste properties within acceptable ranges for viscosity, gel time, set time, heat of hydration, and free liquid. Plastic viscosities ranged from 54 to 580 centipoise (cP). As expected, mixes with lower water/dry mix ratio were more viscous than the mixes with the higher water content. Set times ranged from 21 to 223 hours. Formulations with the higher water/dry mix ratio and higher sodium concentrations had longer set times. Set times greater than 72 hours would require reformulation to reduce hold time prior to disposal. Total heat generation was in the range of 150 to 434 J/g of dry blend material with a trend of higher heat generation for the mixes at 0.6 w/dm compared to those at 0.4 w/dm. Three mixes had free liquid that persisted at 3 d and would require reformulation at lower w/dm to minimize free liquid.

Compressive strengths of the different mixes ranged from 6.6 to 55.4 MPa (960 to 8040 psi). All of the mixes exceeded the target minimum compressive strength of 3.4 MPa (500 psi). As expected, mixes with 5 M Na simulants and the 0.4 w/dm ratio had higher compressive strengths than mixes with 7.8M Na simulants and the 0.6 w/dm ratio.

EPA Method 1311 [7], was conducted to demonstrate that the Cast Stone screening test formulations would meet RCRA land disposal restrictions for hazardous wastes. The results showing the maximum and minimum leachate concentrations across the 26 formulations tested are shown in Table IV. As described previously, the simulants used in the Cast Stone specimens were spiked with only Cr, Pb, Ni, and Cd. Neither Pb nor Cd was detected in any of the TCLP extracts. Chromium and Ni were measured in most but not all of the extracts. As, Ba, and Se were not included in the simulants but were present in the dry materials used to make the Cast Stone. All of the 26 Cast Stone mixes easily met UTS limits.

Table IV. Toxicity Characteristic Leaching Procedure Results

Element	UTS limit, $\mu\text{g/L}$	Reporting Limit, $\mu\text{g/L}$	Minimum	Maximum
Ag	140	<5	<5	<5
As	5000	<10	<5	45.1
Ba	21000	<5	101	1120
Be	1220	<5	<5	<5
Cd (Spike)	110	<5	<5	<5
Cr (Spike)	600	<5	<5	106
Pb (Spike)	750	<10	<10	<10
Hg	25	<0.2	<0.2	<0.2

Ni (Spike)	11000	<5	<5	119
Sb	1150	<20	<20	<20
Se	5700	<10	15.7	68.1
Tl	200	<25	<25	<25

EPA Method 1315 [13] leach tests were conducted for a total of 91 d exposure using DIW leachant. Figure 3 shows the observed diffusivities for Na, NO₃, NO₂, I, Tc, Cr, and U for Cast Stone Mix 5 (Average 7.8 M Na simulant mixed with NW/NW dry blend and a w/dm ratio of 0.4). The figure shows the relative leaching performance of the different constituents with Na, NO₃, NO₂, and I having comparable diffusivities and with Tc, Cr, and U having increasingly lower diffusivities. Results for Tc Leach Index appear in Figure 4. The Tc Leach Index ranged from 9.1 to 11.2 with an average of 10.3. Compared to the Tc leachability index (LI) analyzed in the Tank Closure and Waste Management Environmental Impact Statement (TC&WM EIS) of 8.5 [23] this represents >100X improvement in Tc release rate from the waste form.

Cast Stone Formulation Enhancements

Objectives of these tests were to evaluate additives to improve leaching performance and to investigate differences observed in the screening tests between the SST Blend and the other simulants. Fresh properties were all within acceptable ranges and followed similar trends that were observed in the screening tests.

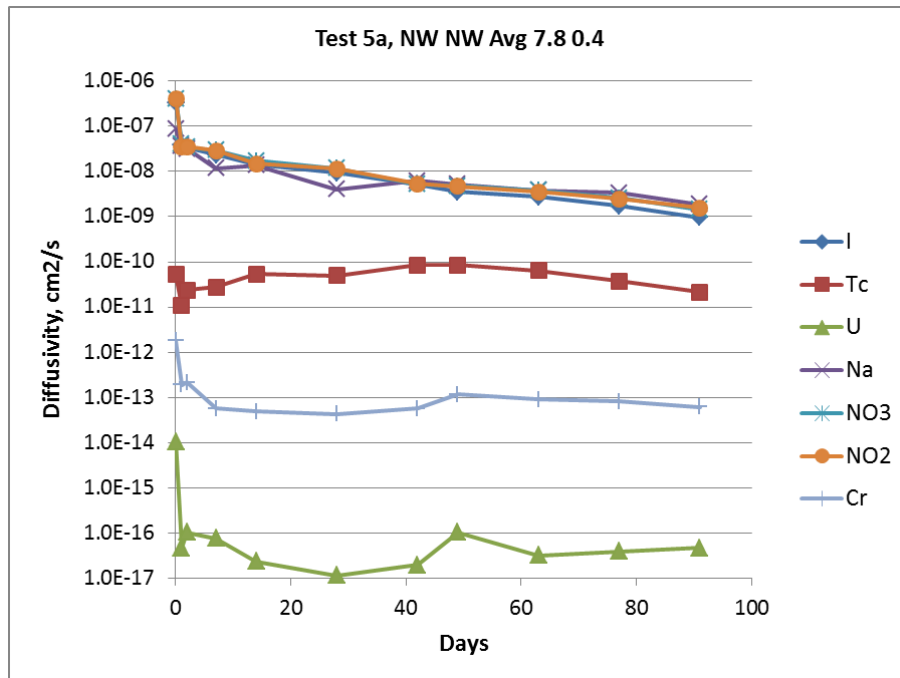


Figure 3. Relative Diffusivities in Cast Stone Screening Tests

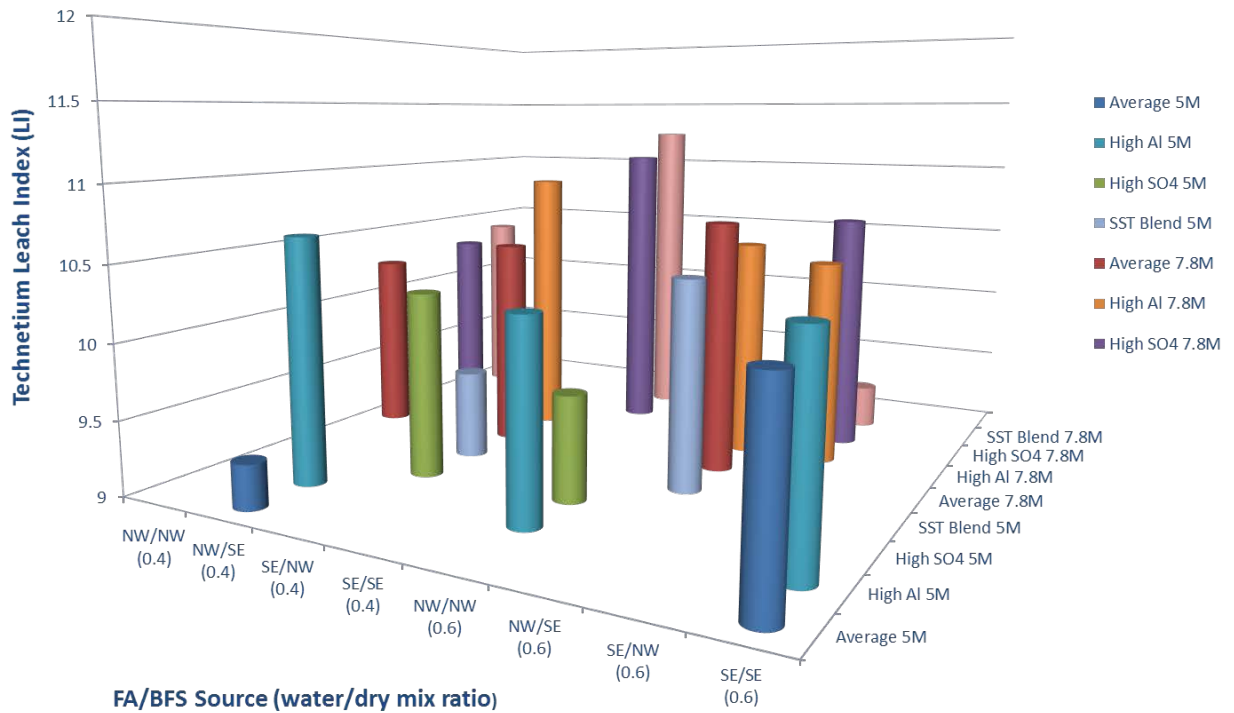


Figure 4. Range of Technetium Diffusivities for Cast Stone Screening Tests

Results of running the EPA Method 1315 Leach Test using DIW as the leachant appear in Table V. The LIs for Na and NO₃ were generally similar. The addition of Xypex may have improved the I leach index in formulations prepared with the HTWOS Average simulant (Mixes 52 and 55) with respect to corresponding mixes that did not contain the admixture (Mixes 51 and 54). No noticeable difference in LIs were noted among the samples prepared with Rheomac SF100 silica fume. Results of leach testing for samples spiked with ⁹⁹Tc appear in the far right column of Table V. The values indicate that for both the HTWOS Average and SST Blend stimulants, Xypex increases the LI by nearly one unit corresponding to a nearly tenfold decrease in Tc observed diffusivity (D_{obs}).

Table V. Average Leach Indices (LIs) for the Augmented Matrix Formulations

Mix #	Salt Solution	FA/BFS Source	Admix	Na	NO ₃	Cr	I	⁹⁹ Tc
51	Average	NW/NW	None	8.1	8.3	>13	8.3	>10.9
52	Average	NW/NW	Xypex Admix C-500	8.1	8.4	>13	9.1	>11.8
53	Average	SE/SE	None	8.3	8.4	>13	8.1	>10.7
54	Average	NW/NW	None	8.1	8.3	>13	8.1	>10.8

55	Average	NW/NW	Xypex Admix C-500	8.0	8.2	>13	9.1	>11.6
56	Average	SE/SE	None	8.1	8.2	>13	9.1	10.4
57	SST Blend	NW/NW	None	8.1	>8.5	>13	7.9	9.7
58	SST Blend	NW/NW	Xypex Admix C-500	8.4	>8.9	>13	8.1	10.8
59	SST Blend	NW/NW	None	8.2	8.3	>13	8.4	9.5
60	SST Blend	NW/NW	Xypex Admix C-500	8.1	8.3	>13	8.1	10.5
61	Average	NW/NW	Rheomac SF100	8.2	8.3	>13	8.6	NA
62	Average	NW/NW	Rheomac SF100	8.1	8.3	>13	8.4	NA
63	SST Blend	NW/NW	Rheomac SF100	8.3	8.4	>13	8.5	NA
64	SST Blend	SE/SE	None	8.4	8.6	>13	8.3	NA
65	SST Blend	NW/NW	Rheomac SF100	8.1	8.3	>13	8.5	NA
66	SST Blend	SE/SE	None	8.1	8.2	>13	8.2	NA

Cast Stone Extended Leach Tests

As noted above extended duration leach tests following the EPA Method 1315 protocol were conducted for durations of 570 to 1040 d. General observations from the results include the following; 1) Leach Indices remained stable throughout the duration of the tests similar to the levels observed between 28 and 63 d in the standard duration EPA 1315 leach test, 2) leach rates for Tc were generally 10X lower in VZPW leachant than in DIW, 3) leach rates for non-sorbing species (e.g., Na, NO₃, NO₂) were only slightly lower in VZPW than in DIW, 4) monoliths containing non-pertechnetate leached Tc about 10X faster in either DIW or VZPW leachant, and 5) all monoliths leached in VZPW showed significant deposition of CaCO₃-polymorphs on the outer surfaces of the monoliths. Details of the extended duration leach testing and results are provided in Serne, et. al. [16] and Asmussen, et. al. [17]

Engineering Scale Demonstration

The primary purpose of the Engineering Scale Demonstration was to show the waste form could be mixed and poured at roughly 1/10th scale (flow rate basis) into a container with the key dimension approximating the width of a standard ISO container (8 ft.) which is commonly used for immobilizing low level radioactive waste in grout. The container was instrumented with thermocouples and all zones within the monolith were below 70°C as the monolith cured. Two sets of core samples were taken from the monolith at approximately 6 mo. and 18 mo. cure time. The results of EPA Method 1315 Leach Testing with DIW leachant for the 18-

mo. core samples along with data from grab samples collected during mixing and pouring of the monolith appear in Table VI.

Table VI. Average Leach Indices for Cast Stone Engineering Scale Demonstration Samples

Temp Zone	Core No.	Sample	Cr	Na	NO ₂	NO ₃
50° C	9 Top	1	9	7.4	7.3	7.2
		2	11.8	7.8	7.7	7.5
	9 Mid	3	8.4	7.1	7.1	6.9
		4	9.8	7.6	7.5	7.4
		5	12.6	6.7	6.7	6.4
	9 Bottom	6	10.3	7.4	7.4	7.2
60° C	10 Top	7	9.5	7.5	7.5	7.4
		8	8.7	7.3	7.4	7.2
	10 Mid	9	8.5	7.1	7	6.8
		10	9.7	7.2	7.1	6.9
		11	11.3	7.4	7.3	7.2
	10 Bottom	12	11.8	6.9	6.9	6.6
70° C	11 Top	13	11.9	7.4	7.3	7.1
		14	9.2	7.2	7.2	7
	11 mid	15	8.4	7.2	7.2	6.9
		16	9.1	7.1	6.9	6.7
		17	11	7.5	7.3	7.2
	11 Bottom	18	12.2	7	7	6.7
		avg	10.2	7.3	7.2	7.0
		Stdev	1.451	0.266	0.252	0.301
		RSD	0.143	0.037	0.035	0.043

Grab Samples (2" x 4" molds)				
Sample	Cr	Na	NO ₂	NO ₃
15	12.5	8	8.5	8.3
16	11.7	8	8.3	8.2
21	10.6	8.3	8.5	8.2
26	9.7	8.3	8.4	8
Avg	11.1	8.2	8.4	8.2
Stdev	1.228	0.173	0.096	0.126
RSD	0.110	0.021	0.011	0.015

Average LIs for Cr and for non-sorbing species were about one unit lower for the large monolith compared to grab samples taken as the monolith was being poured. Variation in the LI values is greater for the large monolith and variation in Cr LI values is greater than for non-sorbing species. There is no apparent trend in LI values with temperature zone. There appears to be some variation with vertical position but no clear trend. Details of the results and data analysis are available in Crawford, et. al. [24].

Cast Stone Testing with Tc and I Getters

The Tc getters tested included Sn(II)Apatite (Sn-A) and potassium metal sulfide (KMS-2) while the iodide getters included Ag-loaded zeolite (Ag-Z) and argentite (Ag₂S). The getters were added to the spiked simulant (PNNL) or real waste (SRNL) in sequences and durations designed to minimize interactions between the getter materials. Results of EPA Method 1315 leach testing of Cast Stone samples made from simulants spiked with Tc and I appear in Table VII. Values presented are averages of the last four leaching intervals for duplicate samples leached for each Batch ID.

The results for Cast Stone made with spiked simulants show that both Sn-A and KMS-2 can increase retention of Tc in Cast Stone when leached in VZPW. Tc LIs were about 1 unit greater than for the Cast Stone with no getter added corresponding to about a 10X reduction in Tc observed Diffusivity. The Tc LIs for

Cast Stone leached in DIW showed no improvement in Tc retention with the addition of Tc getters which underscores the value of using a leachant that more closely resembles the chemical environment expected in the disposal facility. The difference in Tc LIs when leached in VZPW vs. DIW may be related to the buffering capacity of the VZPW as evidenced by lower pH of VZPW leachates [22].

Table VII. Average Leach Indices for Cast Stone with Tc and I getters.

Batch ID	Tc Getter	I Getter	Tc Leach Index		I Leach Index	
			DIW	VZPW	DIW	VZPW
T1	none	none	10.6	11.2	8.0	8.0
T2	Sn-A, 24 hr contact	Ag-Z, 24 hr contact	10.8	11.9	8.1	8.1
T3	KMS-2-SS, 24 hr contact, filter	Ag-Z, 48 hr contact	10.7	12.3	8.2	8.3
T4	KMS-2-SS, 24 hr contact, filter	Ag ₂ S, 48 hr contact	10.7	12.2	8.0	8.0
T5	KMS-2-SS, 48 hr contact	Ag-Z, in dry blend	10.3	12.0	8.0	8.0
T6	KMS-2-SS, 48 hr contact	Ag ₂ S, in dry blend	10.7	12.1	8.0	8.0

The results for Cast Stone made with spiked simulants indicate that no significant increase in I retention was observed at the later leach intervals with either Ag-Z or argentite getters added. No significant difference was also observed between LIs measured in VZPW and DIW leachants. The investigators noted that sulfides from the KMS-2 Tc getter or from the BFS in the Cast Stone formulation could compete with I for association with the Ag-based getters and that AgI itself, although sparingly soluble ($K_{sp} = 8.5 \times 10^{-17}$), could release sufficient Ag to yield the observed LIs. Details and technical rationale for the observed results are provided in Asmussen et. al. [22].

Results from EPA 1315 leach testing of Cast Stone monoliths made from real waste with Tc and I getters added were not available in time for inclusion in this paper but will be included in a future publication.

CONCLUSIONS

The screening tests demonstrated that for the range of parameters studied, the formulations could be processed and would provide acceptable waste forms. All of the Cast Stone mixes had acceptable properties with respect to anticipated waste acceptance criteria for near surface disposal. Compressive strengths well exceeded the 500 psi (3.45 MPa) target. The leachates from the TCLP test easily met treatment standards to address Land Disposal Restrictions for hazardous metals in 40 CFR 268.

EPA Method 1315 Leach Tests were conducted on cured Cast Stone samples for 91 d using DIW leachant to measure observed diffusivities (D_{obs}) for key constituents of concern including Tc, I, U, Cr, Na, NO_3 , and NO_2 . Diffusivities converted to leach indices (LIs) for Na, I, NO_3 , and NO_2 averaged over the 28- to 91-d leach intervals were in the range of 8 to 8.7. Technetium LIs ranged from 9.7 to 11.2 with an average of 10.3. LIs for Cr ranged from 12.0 to 14.1. Uranium was not detected in most of leachates indicating that the U is retained in the Cast Stone and is being minimally released under the conditions of the EPA 1315 leach test. The screening test results indicated that the Cast Stone formulation is robust having minimal variation in properties with varying simulants composition and that higher waste loadings could be achieved than were previously considered practical.

Tests with additives designed to occlude porosity showed promise for improving Tc and I retention in Cast Stone. LIs for both Tc and I with Xypex additive increased by ~1 unit corresponding to a 10X decrease in observed diffusivity when subjected to the EPA Method 1315 leach test with DIW leachant. Extended duration leach tests of Cast Stone samples ranging from 570 to 1040 d exposures indicated that leach rates remained stable throughout the duration of the tests. Leach rates for Tc were generally 10X lower in VZPW leachant than in DIW while leach rates for non-sorbing species (e.g., Na, NO_3 , NO_2) were only slightly lower.

An Engineering Scale Demonstration was conducted at roughly 1/10th scale of a prospective LAW Cast Stone process (1 gpm liquid feed rate). LIs for Cr and non-sorbing species from core samples taken from different locations in the 8.5 ft. diameter by 39 in. high monolith showed noticeable variation (RSDs $LI_{Cr} \sim 14\%$, $LI_{non-sorbing} \sim 4\%$) but LIs were generally about 1 unit lower for monolith core samples compared to grab samples cast in 2 in. x 4 in. cylindrical molds. The latter may have been due to different storage conditions where the where the top surface of the large monolith was exposed to ambient weather while the grab samples were held in covered storage. The low Cr LIs may have been due to much shorter mixing time (<3 min.) compared to 15 min. for laboratory-prepared samples.

Cast Stone tests with Tc and I getters incorporated indicated that the Tc LI could be increased by about 1 unit compared to the control corresponding to a 10X decrease in diffusivity with getter addition of <0.01 wt% of the overall Cast Stone mix in the case of the KMS-2 getter. Ag-based Iodide getters were not effective in tests with Cast Stone possibly due to being reduced by Tc getters or by forming a more thermodynamically stable Ag_2S species through interactions with the sulfide containing BFS, thereby releasing iodide into solution.

REFERENCES

1. Lockrem LL, *Hanford Containerized Cast Stone Facility Task 1-Process Testing and Development Final Report*, RPP-RPT-26742 Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington (2005).
2. A. D. Cozzi, W. E. Daniel, R. E. Eibling, E. K. Hansen, P. G. Heasler, M. J. Lindberg, T. M. Mercier, G. F. Piepel, M. M. Reigel, R. L. Russell, D. J. Swanberg,

- and J H Westsik, Jr., Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Screening Tests, RPP-RPT-55960, Rev. 0, Washington River Protection Solutions LLC, Richland, Washington (2013).
3. Russell RL, JH Westsik Jr, DJ Swanberg, RE Eibling, A Cozzi, MJ Lindberg, GB Josephson, and DE Rinehart. *Letter Report: LAW Simulant Development for Cast Stone Screening Tests*, PNNL-22352, Pacific Northwest National Laboratory, Richland, Washington (2013).
 4. Rassat SD, LA Mahoney, RL Russell, SA Bryan, and RL Sell, *Cold Dissolved Saltcake Simulant Development, Preparation, and Analysis*. PNNL-14194, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington (2003).
 5. Gasper KA, KD Boomer, ME Johnson, GW Reddick, Jr., AF Choho, and JS Garfield, *Recommendation for Supplemental Technologies for Potential Mission Acceleration*, RPP-11261, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington (2002).
 6. Certa PJ, PA Empey, and MN Wells, *River Protection Project System Plan*, ORP-11242, Rev. 6, Washington River Protection Solutions, LLC, Richland, Washington (2011).
 7. EPA Method 1311, Rev. 0, *Toxicity Characteristic Leaching Procedure*, in *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, EPA SW 846, U.S. Environmental Protection Agency, Washington, D.C. (1992)
 8. Mattigod SV, JH Westsik, Jr, CW Chung, MJ Lindberg, and KE Parker, *Waste Acceptance Testing of Secondary Waste Forms: Cast Stone, Ceramicrete and DuraLith*. PNNL-20632, Pacific Northwest National Laboratory, Richland, Washington (2011).
 9. Rapko BM, SI Sinkov, and TG Levitskaia, *Removal of ¹³⁷Cs from Dissolved Hanford Tank Saltcake by Treatment with IE-911*. PNNL-14250, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington (2003).
 10. ASTM D6103-2004, *Standard Test Method for Flow Consistency of Controlled Low Strength Material (CLSM)*. ASTM International, West Conshohocken, Pennsylvania.
 11. ASTM C191-2008, *Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle*. ASTM International, West Conshohocken, Pennsylvania.
 12. ASTM C1679-2009, *Standard Method for Measuring Hydration Kinetics of Hydraulic Cementitious Mixtures Using Isothermal Calorimetry*. ASTM International, West Conshohocken, Pennsylvania.
 13. EPA Method 1315, *Mass Transfer Rates of Constituents in Monolith or Compacted Granular Materials Using a Semi-Dynamic Tank Leaching Test*, U.S. Environmental Protection Agency, Washington, D.C. (2013).
 14. ASTM C39-2012, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*, ASTM International, West Conshohocken, Pennsylvania.
 15. Cozzi, AD, KM Fox, EK Hansen, and KA Roberts, *Supplemental Immobilization of Hanford Low-Activity Waste: Cast Stone Augmented Formulation Matrix Tests*, SRNL-STI-2014-00619, Rev. 0, Savannah River National Laboratory, Aiken, South Carolina (July 2015).

16. Serne, RJ, DC Lanigan, JH Westsik Jr, BD Williams, HB Jung, and G Wang, *Extended Leach testing of Simulated LAW Cast Stone Monoliths*, PNNL-24297, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington (June 2016).
17. Asmussen, RM, CI Pearce, KE Parker, B Miller, B Lee, E Buck, N Washton, M Bowden, AR Lawter, E McElroy, and RJ Serne, *Solid State Characterizations of Long-Term Leached Cast Stone Monoliths*, PNNL-25578, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington (September 2016).
18. Cozzi, AD, MD Fowley, EK Hansen, RE Eibling, KM Fox, DH Miller, and MR Williams, *Engineering Scale Demonstration of a Prospective Cast Stone Process*, SRNL-STI-2014-00428, Revision 0, Savannah River National Laboratory, Aiken, South Carolina (September 2014).
19. RM Asmussen, JJ Neeway, AR Lawter, TG Levitskaia, WW Lukens and N Qafoku, "The Function of Sn(II)-Apatite as a Tc Immobilizing Agent," *Journal Of Nuclear Materials*, 480, 393-402 (2016).
20. JJ Neeway, RM Asmussen, AR Lawter, ME Bowden, WW Lukens, D Sarma, BJ Riley, MG Kanatzidis and NP Qafoku, "Removal of TcO₄-from Representative Nuclear Waste Streams with Layered Potassium Metal Sulfide Materials," *Chemistry of Materials*, 28, 3976-3983 (2016).
21. RM Asmussen, JJ Neeway, AR Lawter, A Wilson and N Qafoku, "Silver Based Getters for 129-I Removal from Low Activity Waste," *Radiochimica Acta*, Accepted, DOI: <http://dx.doi.org/10.1515/ract-2016-2598> (2016).
22. Asmussen, RM, CI Pearce, AR Lawter, JJ Neeway, B Miller, B Lee, N Washton, J Stephenson, RE Clayton, M Bowden, E Buck, E Cordova, BD Williams, and NP Qafoku, *Getter Incorporation into Cast Stone and Solid State Characterizations*, PNNL-25577, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington (September 2016).
23. DOE, *Final Tank Closure and Waste Management Environmental Impact Statement for the Hanford Site, Richland, Washington*, DOE/EIS-0391, U.S. Department of Energy, Washington, D.C. (2012).
24. Crawford, CL, AD Cozzi, and KA Hill, *Analysis of Monolith Cores from an Engineering Scale Demonstration of a Prospective Cast Stone Process*, SRNL-STI-2015-00678, Revision 0, Savannah River National Laboratory, Aiken, South Carolina (June 2016).